

Ch 6 Chemical Bonding

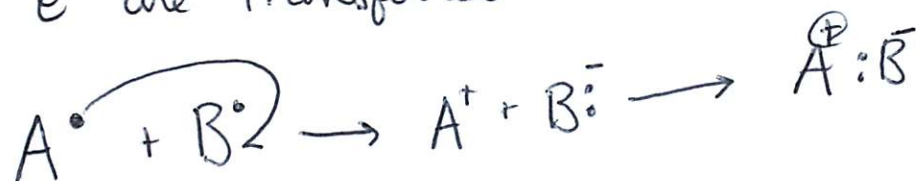
Basis for all structures in life Why things stay together

Chemical bond → link between atoms that results from ~~mutual~~ mutual attraction of their nuclei for e^-

Types of bonds → (nonmetal + metal) (metal + polyatomic ion)

1. Ionic bonds - attraction between pos + neg ions resulting in formation of a chemical bond.

e^- are transferred



Ex NaCl

2. Covalent Bonding - Chemical Bond resulting in sharing of electrons
(2 non metals)
(polyatomic ion)



Bonds are seldom completely ionic or covalent

(2)

That Beautiful Grey area

The for Ionic bonds we consider E-neg

The larger difference in Electronegativity,

More ionic the bond is

The e^- will spend more time around the
more e^- negative atom

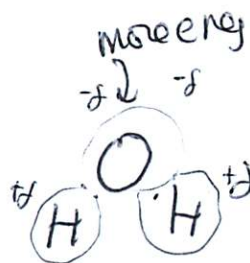
Degrees of covalent bonds

↳ ~~less ionic characters~~ nonpolar covalent

Polar covalent → bond where united atoms ~~are~~
have unequal attraction for e^-

Polar → means separation of charge.

So some ~~have~~ covalent bonds have
slight separation of charge → H_2O



Non polar covalent - bond where e^- are shared equally
between atoms.

~~Measure~~ Tell by using following chart

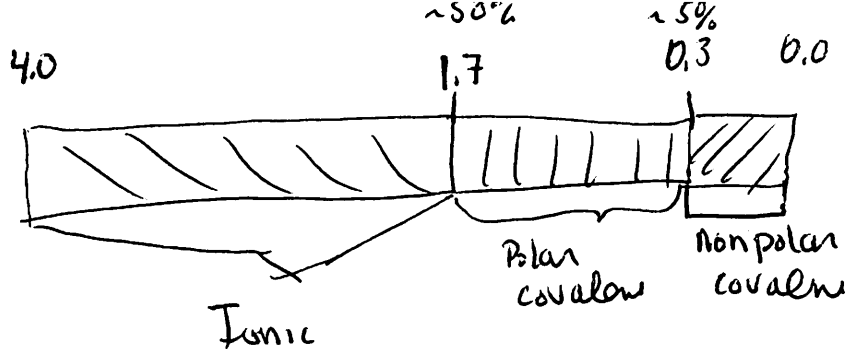


Fig 6-2

To determine types of bond
subtract e-neg and if between

4.0 - 1.8 Ionic

1.7 - 0.3 Polar Covalent

0.3 - 0.0 non polar covalent

Ex Sulfur e-neg = 2.5

Type of bond w/ H?
(2.1)

2.5 - 2.1 = .4 Polar covalent Sulfur

" C_s? = 2.5 - (.7) = 1.8 Ionic Sulfur
(0.7)

Cl = 3.0 - 2.5 = .5 Polar cov Cl
(3.0)

Between B(2.0) + H(2.1)

2.1 - 2.0 = 0.1 nonpolar

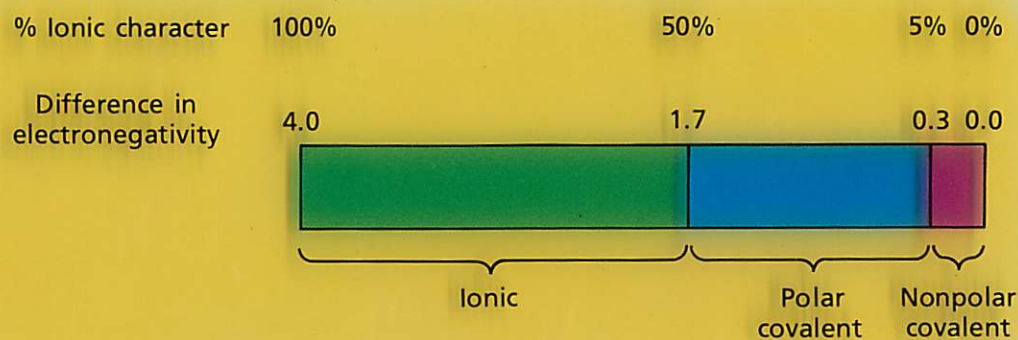


Figure 6-2

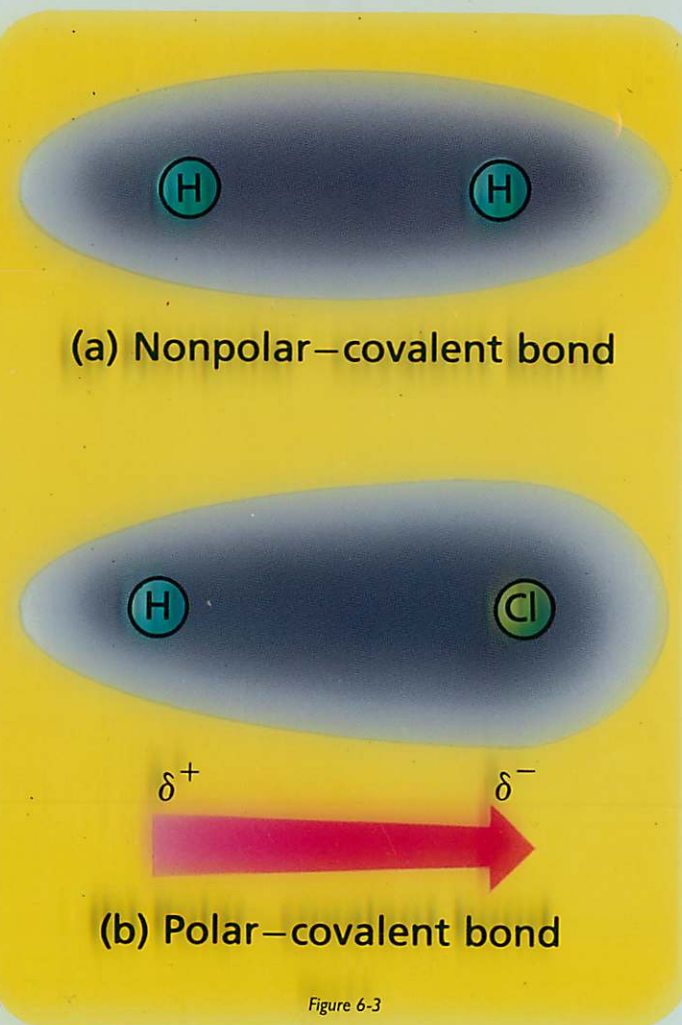
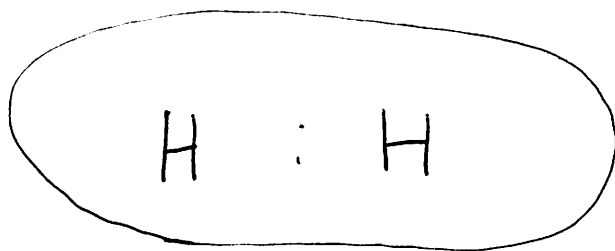


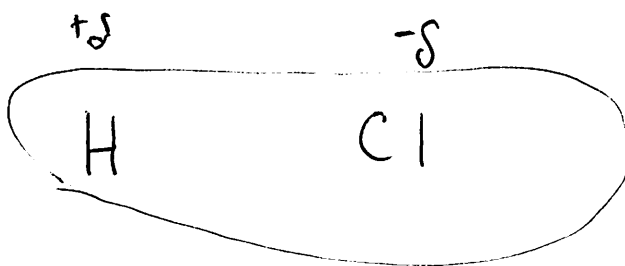
Figure 6-3

Density of e^- between Polar + Nonpolar

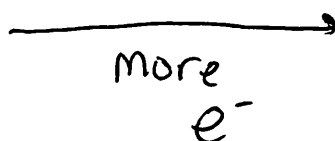
④



Non polar
equal distribution



Polar



Why do bonds form?

b/c of decrease in PE

If ϵ given off means bond is more favorable. Anytime PE is lowered that state is favored

pg 164 Q2,3,4

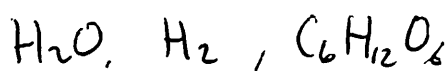
6.2 Covalent Bonding + Molecular Comp

5

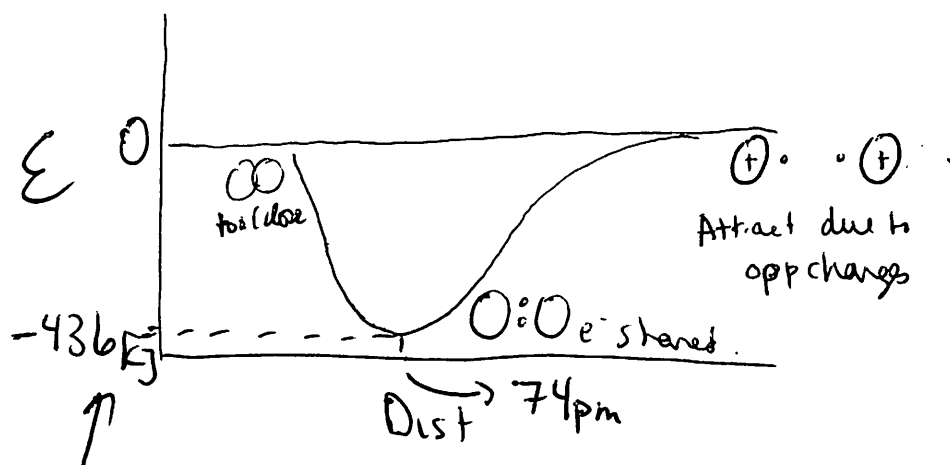
Molecule \rightarrow group of 2 or more atoms held together by covalent bonds and able to exist independently

diatomic molecule \rightarrow compound w/ 2 atoms

Chemical formula - shorthand rep of the composition of a substance using atomic symbols + [#]subscripts



How a bond forms? Energy diagram



E_{released}

436 kJ of E_{released}

\hookrightarrow Release of E ~~low~~ puts molecule @ lower E than atoms stable

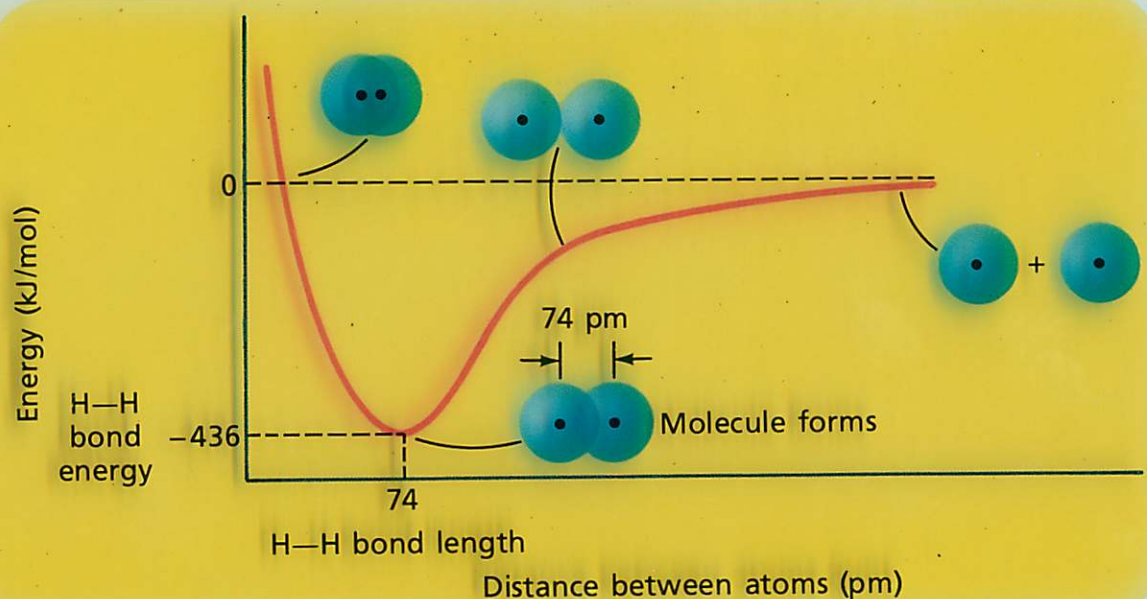


Figure 6-4

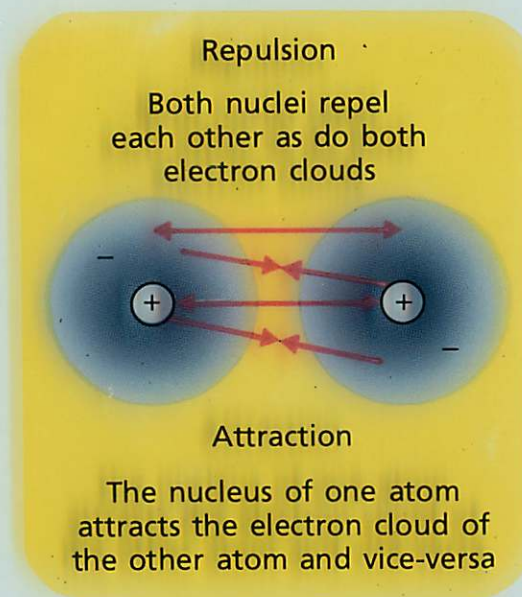


Figure 6-5

Bond Length \rightarrow Avg dist b/tween 2 bonded atoms

\hookrightarrow Varies w/ compounds (why? - space orbital filled)
(E-neg)

Bond energy \rightarrow energy required to Break a chemical Bond.

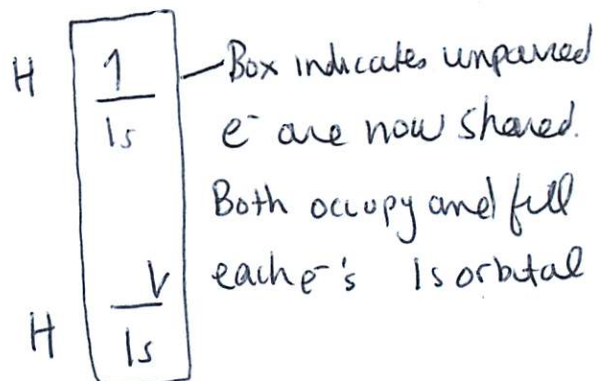
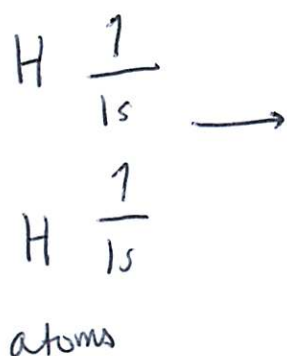
\hookrightarrow given as KJ/mol.

to break an H-H bond it take 436 KJ/mol

How much does it take to break for 1 molecule?

BE larger as Bond Length shorter

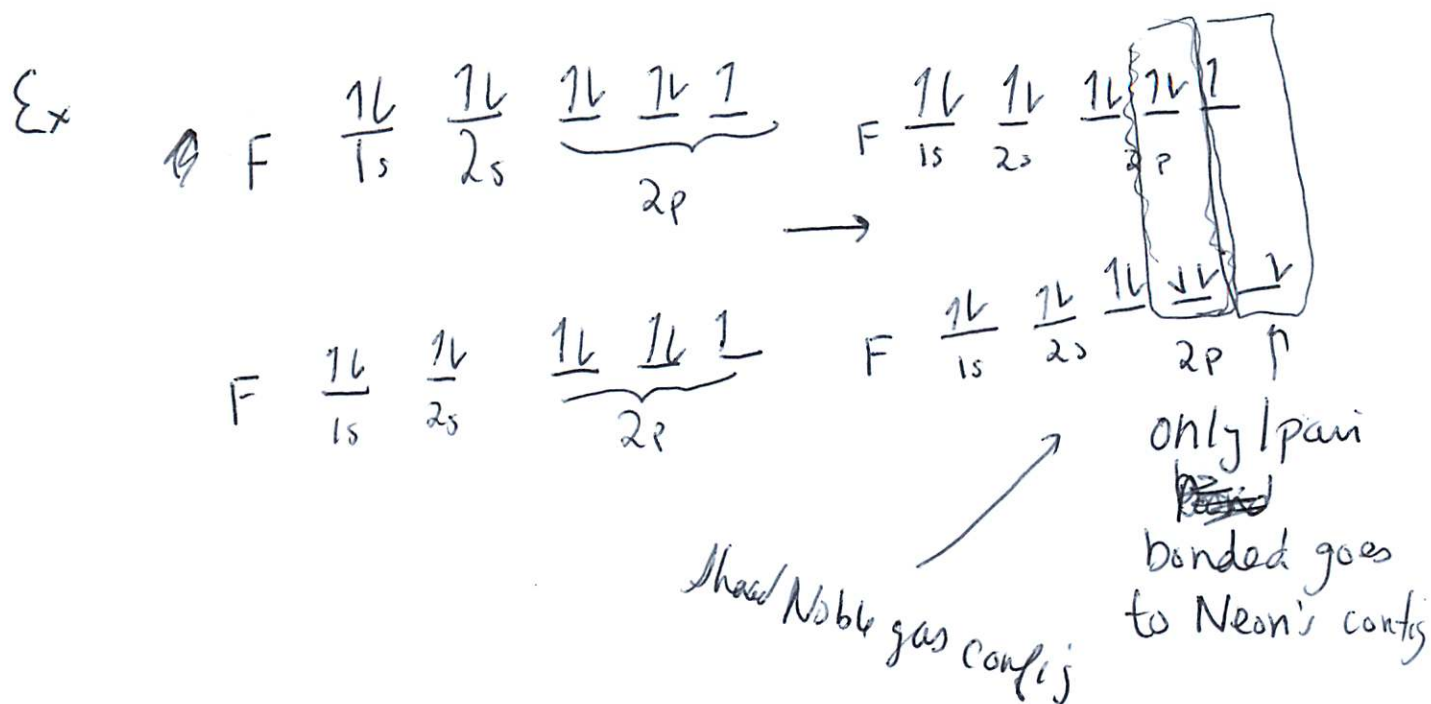
What happens \rightarrow Look @ orbital notation to understand



B/c e^- are shared both 1s orbitals are filled and each H atom has stable $1s^2$ config (He)

the same happens for the other diatomic atoms

N, O, F, Cl, Br, I, At



These follow something called the Octet Rule

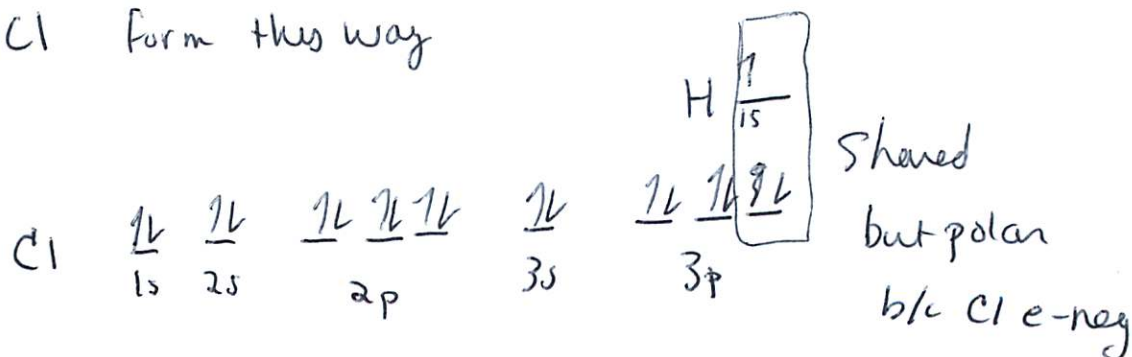
Octet Rule → compounds form so that each atom by either gaining losing or sharing an e^- has an octet of e^- in its highest E level

Exceptions BF_3 only 3 pairs
 PCl_5 SF_6 → b/c d orbitals

↳ There are exceptions though

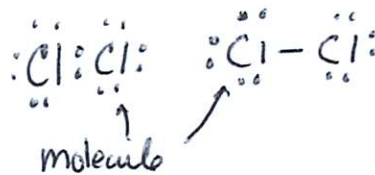
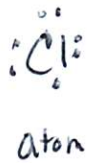
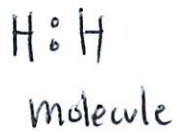
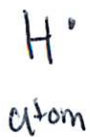
Discuss Later

HCl form this way



8

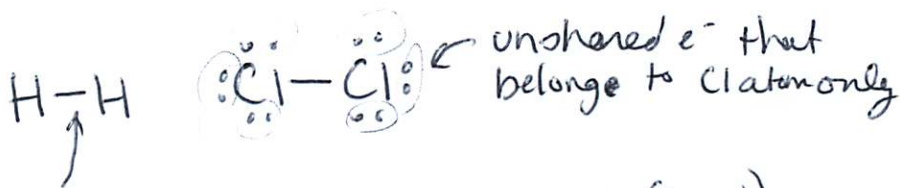
↳ e^- dot for molecules



Bond shown as line

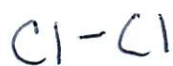


Lewis Structure



Shared e^- are represented as dash (bond)

structural formula no dots for e^- only show bonds



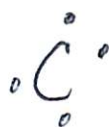
Drawing Lewis X-funcs

ing Lewis structures

Draw Iodomethane CH_3I (C is central)

1. How many elements present, which ones
1 C, 3 H, 1 I

- 2 Draw e^- dot for each



skier →

3 Determine # of valence e^- to be combined

9

$$C \quad 1 \times 4e^- = 4e^-$$

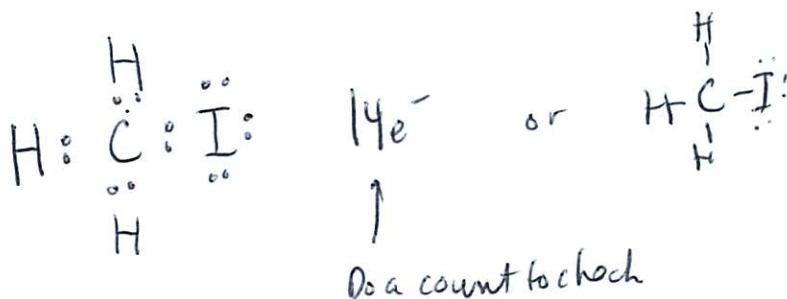
$$I \quad 1 \times 7e^- = 7e^-$$

$$H \quad 3 \times 1e^- = \frac{3e^-}{14e^-}$$

4 Arrange atoms to form skeleton structure w/ most e^- pos
element central (C always central)
connect atoms w/ e^- dot pairs



5 Add unshared pairs of e^- so each nonmetal atom (not H)
has $8e^-$

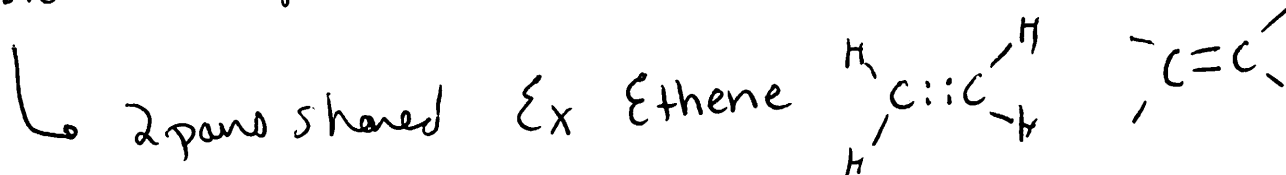


Ex Lewis structure for NH_3 , ICl , SiF_4

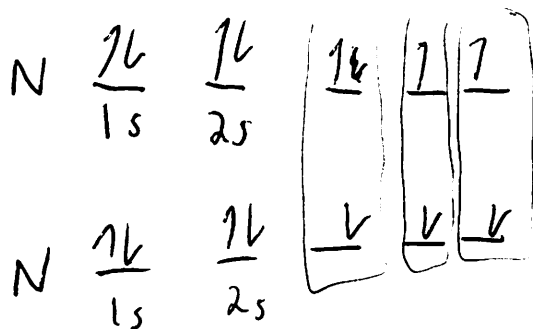
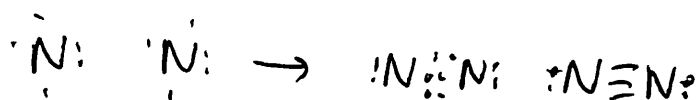
Rules of thumb → N 3 bonds, lone pair (unless (+) 4 bonds)
O 2 " 2 " " unless (-) → 1 bond
H only 1 bond no free e^-
C always central, Always 4 bonds

Multiple Bonds

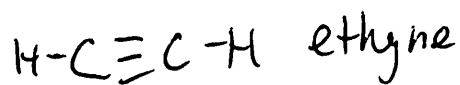
Double and Triple bonds



Triple N can form triple bonds (3 pairs shared) Take more energy to break multiple bonds



C forms triple bonds too



multiple bonds are possible

if get too many valence e^- when drawing Lewis structure

Do multiple bonds

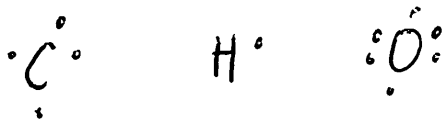
Multiple

formalin antiseptic

 CH_2O

11

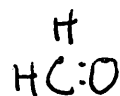
Lewis dot



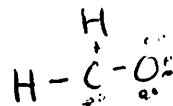
#valence

$$\begin{array}{r} \text{C } 1 \times 4e^- \\ \text{H } 2 \times 1e^- \\ \text{O } 1 \times 6e^- \\ \hline 12e^- \end{array}$$

skeleton



add valence



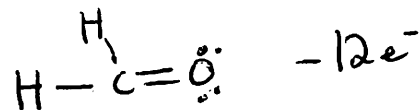
count

$$\frac{14e^-}{\text{too many?}}$$

Double Bond

subtract 1 lone pair
until get correct #.

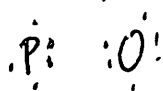
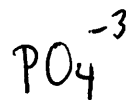
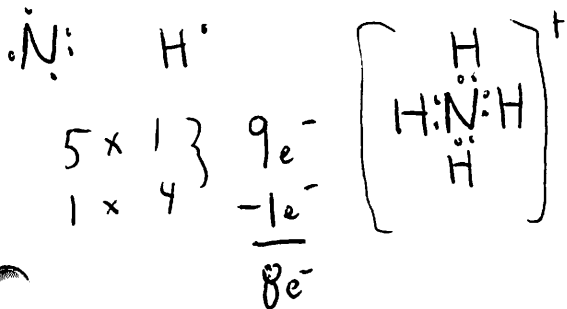
move another pair b/tween C and O,
to get multiple bond

Ex CO_2 , HCN

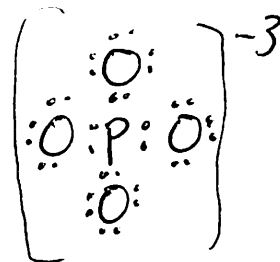
Polyatomic Ions - charged group of covalently bonded e^-

Poly to draw Lewis Xtreme of. subtract (if posion) or add (if neg)

when we count e^-



$$\begin{array}{r} 5 \times 1 \\ 6 \times 4 \end{array} \left. \vphantom{\begin{array}{r} 5 \times 1 \\ 6 \times 4 \end{array}} \right\} \begin{array}{r} 29e^- \\ + 3e^- \\ \hline 32e^- \end{array}$$



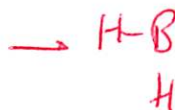
pg 174 04, 5

Octet rule exceptions

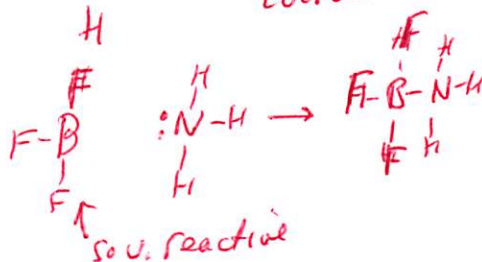
Resonance → ~~Single rule represented by more than 1 Lewis x-ture~~
~~several bonds occurring and changing~~
 leads to what is called contributing x-tures

Ex. Ozone, carboxylic acid (acetate) Carbonate

fewer than 8 val e⁻



picks up octet pair
 from other compound
 coordinate covalent



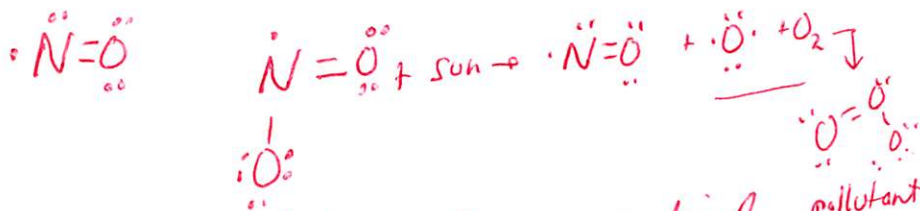
More than 8 val e⁻

↳ use d orbitals for bonding (if available)

NH_3 - N-3 bonds but PF_5 → atoms can accommodate more pairs b/c d-orbital

Draw ~~SOCl₂~~ SF_6 , CF_4^-

free radicals → 1 free unpaired e⁻ NO , NO_2



Very reactive → e⁻ needs pair so reacts to create more radicals
 can destroy ~~body~~ organisms/other molecules

In solids, these Ionic compounds form crystal lattices
see fig 6-10. B/c charges are like they are

The attraction of these charges in solid give them
very high, MT, BP.

Na melts @
Cl melts @
NaCl melts @

$\text{NaCl} \rightarrow \text{BP } 801^\circ\text{C}$
 $\text{BP } 1413^\circ\text{C}$

$\text{SiO}_2 \text{ melts @ } 186^\circ\text{C}$

Ionic forces are very strong - Hold them packed tightly together

Dissolve in water easily b/c Polarity of H_2O
make good conductors

pg 179 Q2

~~Give Criss cross whole~~

~~white out charges though~~

~~Show Criss Cross Method.~~

3rd Type of Bonding Metallic Bonding

↳ Metals → great conductors, malleable
↳ suggest mobility of e^-

Have vacant p + d orbitals @ their disposal
easily give up e^- , (low IE), do not attract e^- (low Energy)

Valence e^- are given up and shared. They are free to move about
and do not stay localized to one atom.

Called an e^- sea

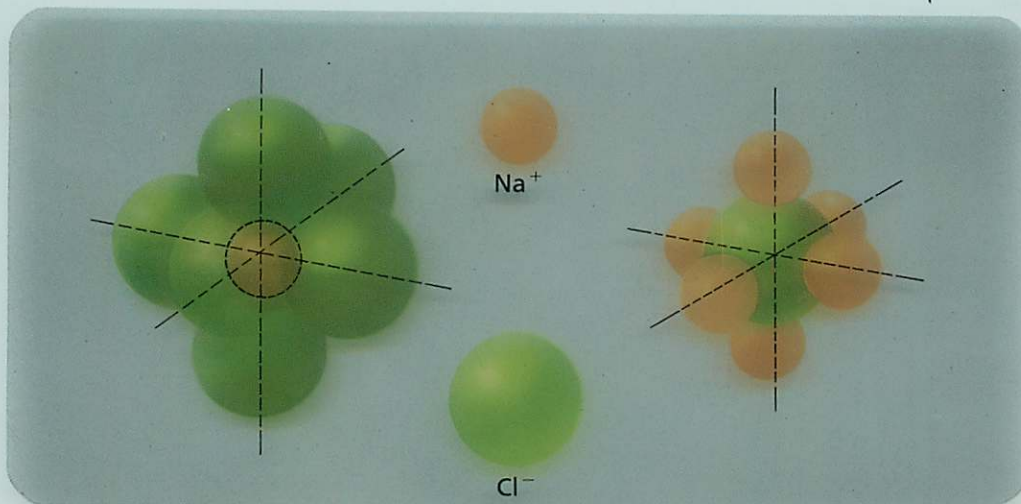


Figure 6-9

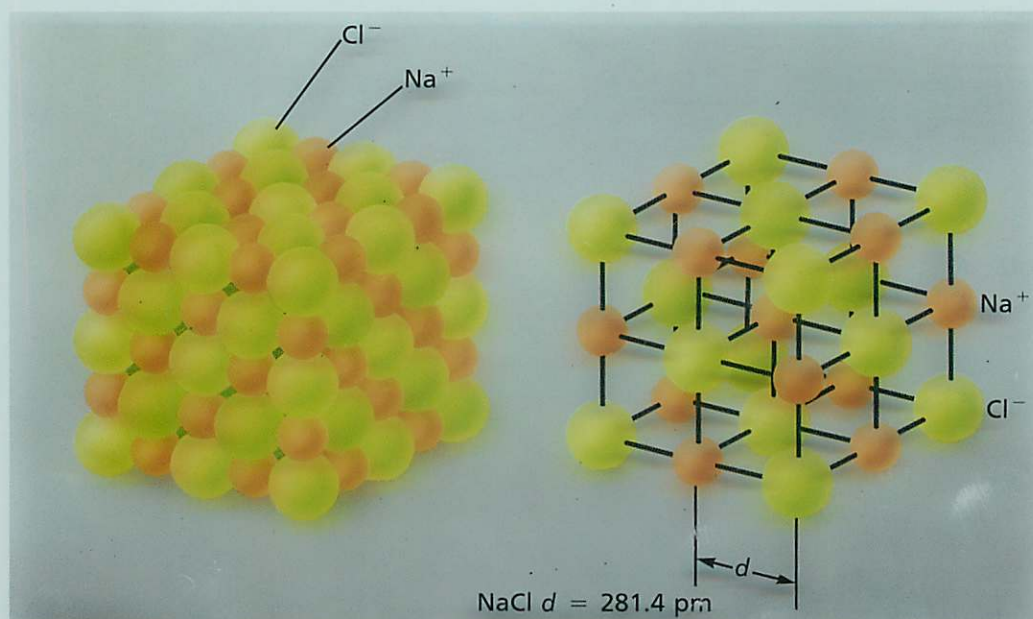
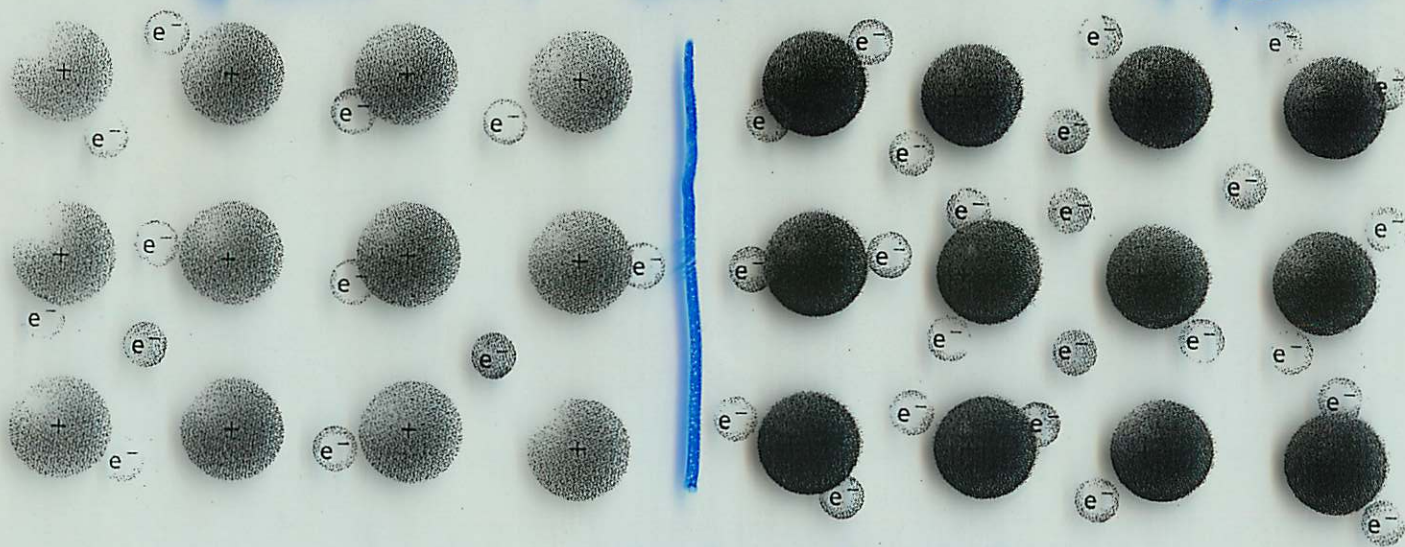


Figure 6-10

"Sea of electrons" fig 6.14



e^- are delocalized
they do not belong to any 1 atom

Strength of ~~charge~~ bond depends e^- shared + # of valence e^-

14

Bond strength measured by how much heat it takes to vaporize a mole of that metal (kJ/mol)

↳ effect this - charge + # of valence e^-

e^- sea explains high conductivity e^- carry charge
" heat conduction e^- move fast carrying heat

Malleability + Ductility

↳ B/c the bonds are not ~~are~~ brittle they can slide past one another w/o breaking bonds

181 Q 2+3

Columns for USE R Table

molec type ^{uns lone} ^g ^{e-pairs} ^{on central} ^{atom} ^{geom} Type Bond < Ex ^{3-b} ^{2-b} Lewis & lone

Properties of compounds depend on 2 things

bonding \rightarrow ionic, covalent, etc

geometry - use 2 models which both fit
different situations equally well

1 VSEPR - valence shell e^- pair repulsion

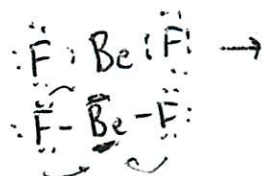
\hookrightarrow geometry of compounds based on electrostatic repulsion - Bonds angle themselves in lowest energy possible (as far apart as possible)

In compounds w/ 2 atoms

H_2 easy $\rightarrow H:H, H-H$ linear (A_2)

many varieties in ones w/ 3 ^{or more} atoms

BeF_2



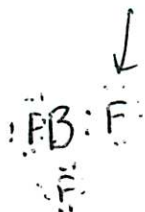
0 lone e^-

Type of mol
 AB_2



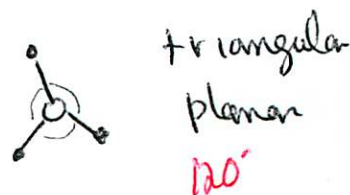
equal repulsion

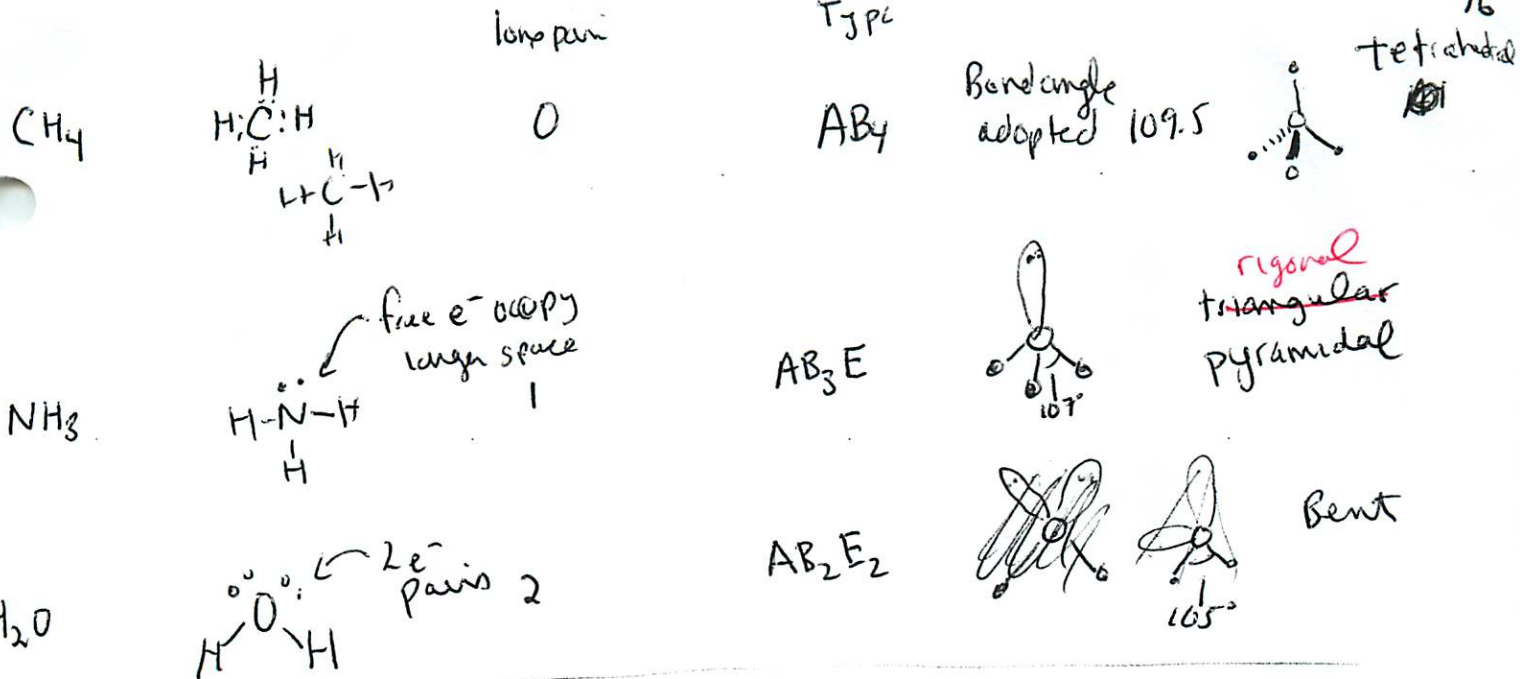
BF_3
 ~~$SnCl_4$~~



0

AB_3

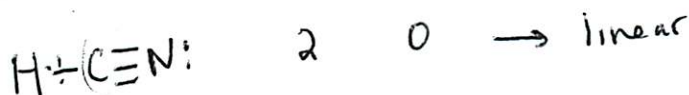




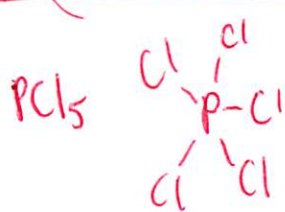
to use table 6-7 it is necessary to know Lewis X-type
classify it to # of bonds around central atom

what type of bond does HCN + H₂CO have

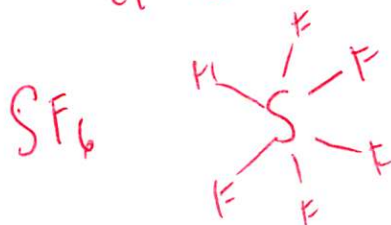
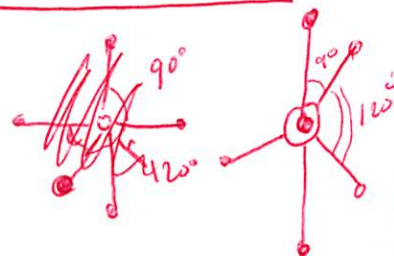
HCN



3 0 → triangular planar



AB₅ trigonal bipyramidal



AB₆ Octahedral

90°

Hybridization

17

VSEPR - reveals no relationship between geometry of molecules and orbitals occupied by bonding e^-

↳ Hybrid Theory accounts for the

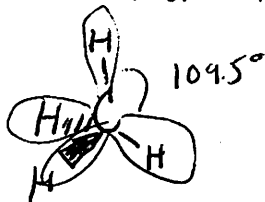
Hybridization - orbitals of equal energy produced by the combination of 2 or more orbitals of the same atom

orbitals produced = # of orbitals used

1s + 3 p make $4sp^3$ hybrids

↳ oriented tetrahedrally

E. CH_4



Explains $NH_3 + H_2O$ bonding as well

Can also have hybrid of only 2 orbitals $s, p \rightarrow sp \rightarrow \infty$ linear
" 3 orbitals sp^2 planar

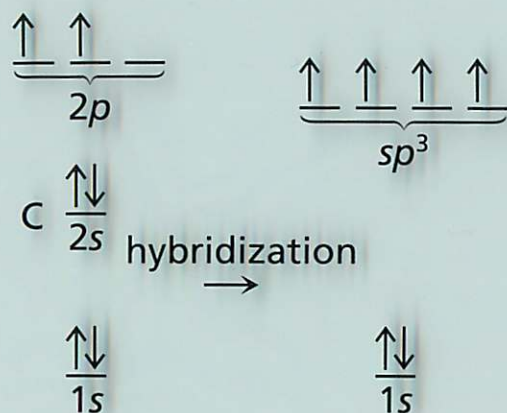


Figure 6-18

TABLE 6-5 GEOMETRY OF HYBRID ORBITALS


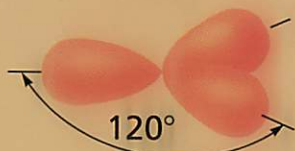
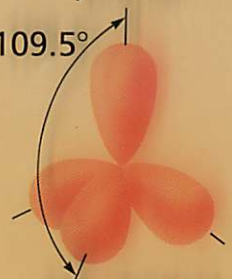
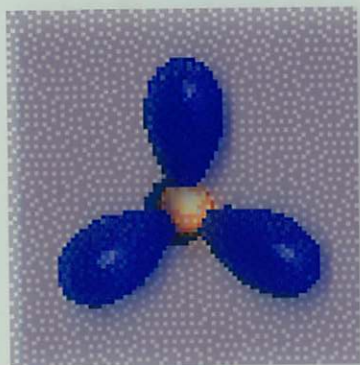
Atomic Orbitals Hybridization	Type of Hybridization	Number of Hybrid Orbitals	Geometry
s, p	sp	2	 180° linear
s, p, p	sp^2	3	 120° planar
s, p, p, p	sp^3	4	 109.5° tetrahedral

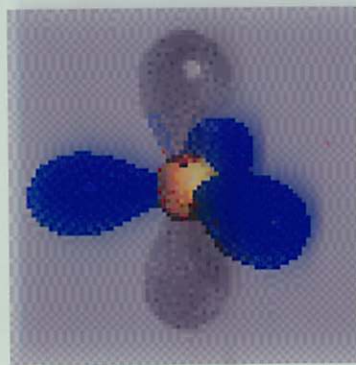
Table 6-5

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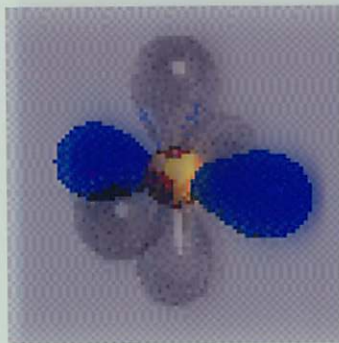
Hybridization



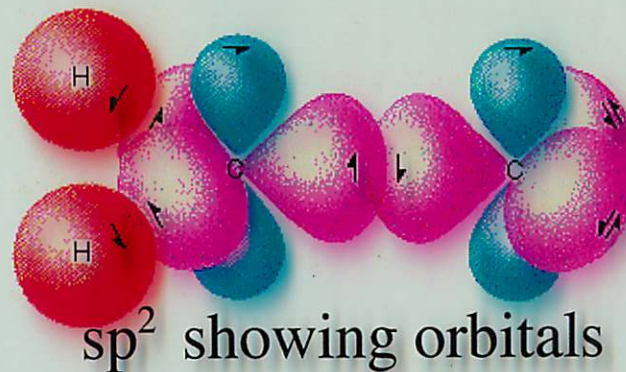
sp^3



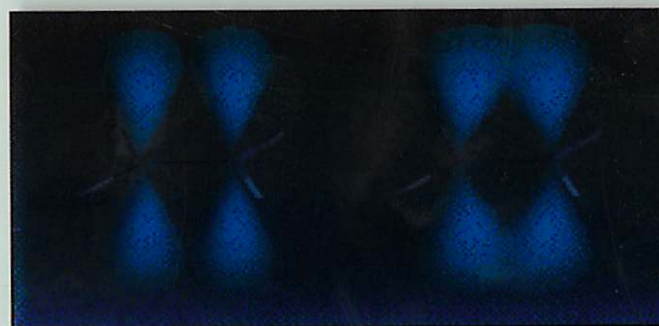
sp^2



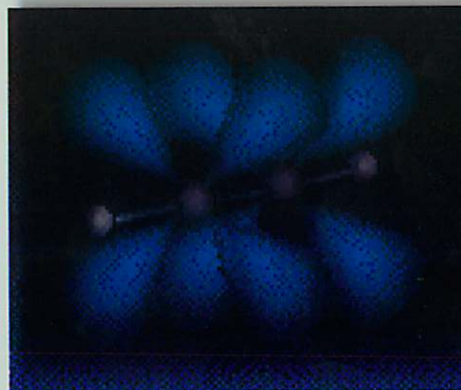
sp



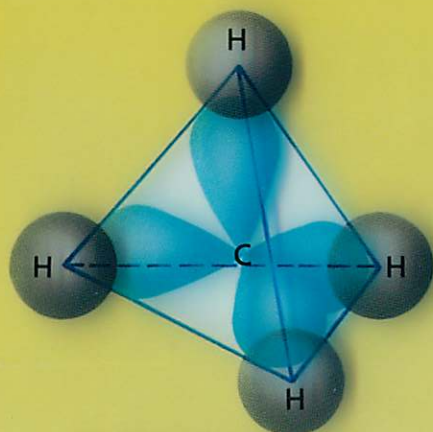
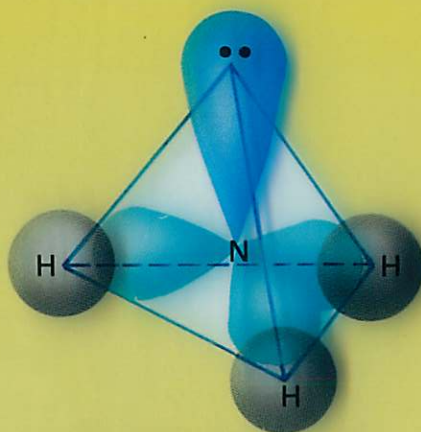
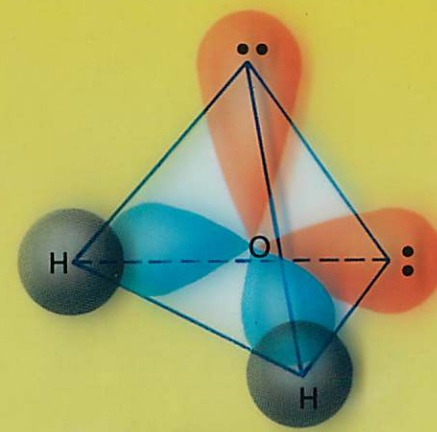
sp^2 showing orbitals



sp^2 hybridization in ethene



sp hybridization in ethyne

(a) Methane (CH₄)(b) Ammonia (NH₃)(c) Water (H₂O)

Hybridization — accounts for geometry + what is happening to the orbitals.

what takes place — s + p orbitals fuse to make hybrid orbitals

s orbital + 3 p orbitals — make 4 sp^3 orbitals

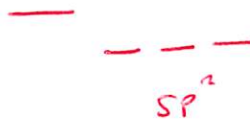


4 σ sigma bond

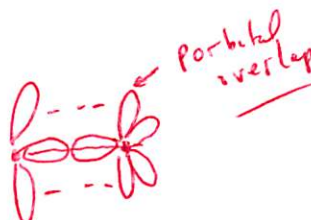
in all 4 directions



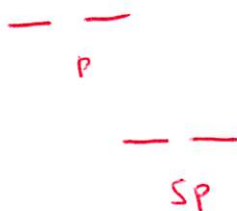
s orbital + 2 p \rightarrow 3 sp^2



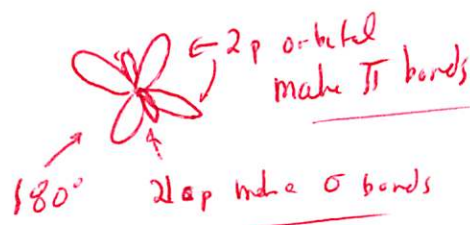
Double Bonding



sp hybridization $1s, 1p \rightarrow 2sp$



Triple bonding



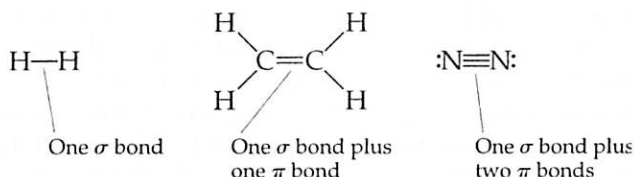
Show overheads of geometries

9.6 Multiple Bonds

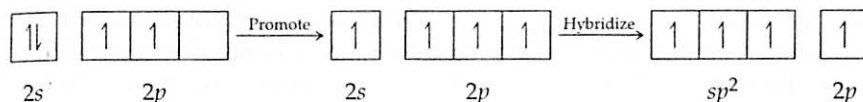
In the covalent bonds that we have considered thus far, the electron density is concentrated symmetrically about the line connecting the nuclei (the *internuclear axis*). In other words, the line joining the two nuclei passes through the middle of the overlap region. These bonds are all called **sigma (σ) bonds**. The overlap of two *s* orbitals as in H_2 [Figure 9.11(a)], the overlap of an *s* and a *p* orbital as in HCl [Figure 9.11(b)], the overlap between two *p* orbitals as in Cl_2 [Figure 9.11(c)], and the overlap of a *p* orbital with an *sp* hybrid orbital as in BeF_2 (Figure 9.14) are all examples of σ bonds.

To describe multiple bonding, we must consider a second kind of bond that results from the overlap between two *p* orbitals oriented perpendicularly to the internuclear axis (Figure 9.19 ►). This sideways overlap of *p* orbitals produces a **pi (π) bond**. A π bond is a covalent bond in which the overlap regions lie above and below the internuclear axis. Unlike a σ bond, in a π bond there is no probability of finding the electron on the internuclear axis. Because the total overlap in the π bonds tends to be less than that in a σ bond, π bonds are generally weaker than σ bonds.

In almost all cases, single bonds are σ bonds. A double bond consists of one σ bond and one π bond, and a triple bond consists of one σ bond and two π bonds:



To see how these ideas are used, consider ethylene, C_2H_4 , which possesses a $\text{C}=\text{C}$ double bond. The bond angles in ethylene are all approximately 120° (Figure 9.20 ►), suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.15) to form σ bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after sp^2 hybridization one electron remains in the *unhybridized 2p* orbital:



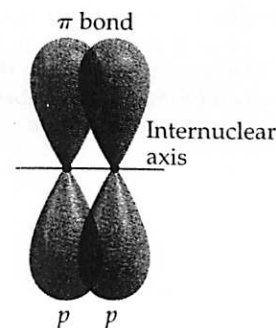
The unhybridized $2p$ orbital is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.

Each sp^2 hybrid orbital on a carbon atom contains one electron. Figure 9.21 ▼ shows how the four $\text{C}-\text{H}$ σ bonds are formed by overlap of sp^2 hybrid orbitals on C with the $1s$ orbitals on each H atom. We use eight electrons to form these four electron-pair bonds. The $\text{C}-\text{C}$ σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. The C_2H_4 molecule has a total of 12 valence electrons, 10 of which form the one $\text{C}-\text{C}$ and the four $\text{C}-\text{H}$ σ bonds.

The remaining two valence electrons reside in the unhybridized $2p$ orbitals, one electron on each of the carbon atoms. These $2p$ orbitals can overlap with one another in a sideways fashion, as shown in Figure 9.22 ►. The resultant electron density is concentrated above and below the $\text{C}-\text{C}$ bond axis; this is therefore a π bond (Figure 9.19). Thus, the $\text{C}=\text{C}$ double bond in ethylene consists of one σ bond and one π bond.

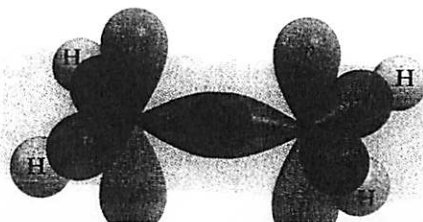
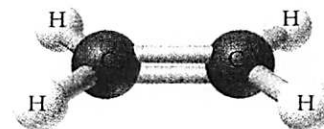
Although we cannot experimentally observe a π bond directly (all we can observe are the positions of the atoms), the structure of ethylene provides strong support for its presence. First, the $\text{C}-\text{C}$ bond length in ethylene (1.34 \AA) is much shorter than that in compounds with $\text{C}-\text{C}$ single bonds (1.54 \AA), consistent with

H Handout



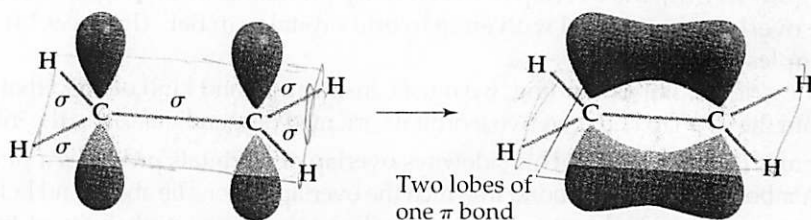
▲ **Figure 9.19** Formation of a π bond by overlap of two *p* orbitals. The two regions of overlap constitute one π bond.

▼ **Figure 9.20** The molecular geometry of ethylene, C_2H_4 .



▼ **Figure 9.21** Hybridization of carbon orbitals in ethylene. The σ bonding framework is formed from sp^2 hybrid orbitals on the carbon atoms. The unhybridized $2p$ orbitals on the C atoms can be used to make a π bond.

► **Figure 9.22** The π bond in ethylene is formed by overlap of the unhybridized $2p$ orbitals on each C atom. The electron density in the π bond is above and below the bond axis, whereas in the σ bonds, the electron density lies on the bond axes. The two lobes constitute one π bond.



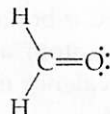
the presence of a stronger $\text{C}=\text{C}$ double bond. Second, all six atoms in C_2H_4 lie in the same plane. Only when the two CH_2 fragments lie in the same plane can the $2p$ orbitals that comprise the π bond achieve a good overlap. If the π bond were not present, there would be no reason to expect the two CH_2 fragments of ethylene to lie in the same plane. Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

Triple bonds can also be explained by using hybrid orbitals. Consider acetylene, C_2H_2 , a linear molecule containing a triple bond: $\text{H}-\text{C}\equiv\text{C}-\text{H}$. The linear geometry suggests that each carbon atom uses sp hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom then has two remaining unhybridized $2p$ orbitals at right angles to each other and to the axis of the sp hybrid set (Figure 9.23 ▼). These p orbitals overlap to form a pair of π bonds. Thus, the triple bond in acetylene consists of one σ bond and two π bonds.

Although it is possible to make π bonds from d orbitals, the only π bond that we will consider is that formed by the overlap of p orbitals. This π bond can form only if unhybridized p orbitals are present on the bonded atoms. Therefore, only atoms having sp or sp^2 hybridization can be involved in such π bonding. Further, double and triple bonds (and hence π bonds) are more common in molecules with small atoms, especially C, N, and O. Larger atoms, such as S, P, and Si, form π bonds less readily.

SAMPLE EXERCISE 9.6

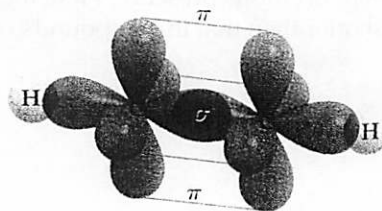
Formaldehyde has the following Lewis structure:



Describe the bonding in formaldehyde in terms of appropriate hybridized and unhybridized orbitals.

Solution Using the VSEPR model, we would predict the bond angles around C to be about 120° (trigonal planar geometry). This geometry suggests sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two $\text{C}-\text{H}$ and one $\text{C}-\text{O}$ σ bonds to C. There remains an unhybridized $2p$ orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

► **Figure 9.23** Formation of two π bonds in acetylene, C_2H_2 , from the overlap of two sets of unhybridized carbon $2p$ orbitals.



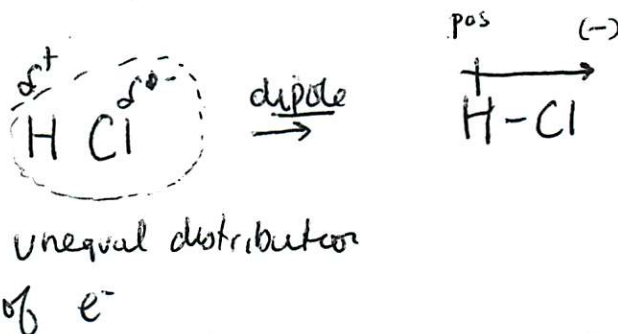
Inter molecular forces - forces of attraction between molecules

↳ weaker forces than those that bond atoms in molecules

Strongest IM force → between polar molecules

Dipole - Equal but opposite charges separated by a short distance

Like HCl

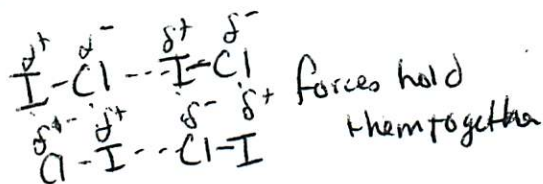


↳ Dipole-dipole forces - attractive forces between polar molecules -34.6°C

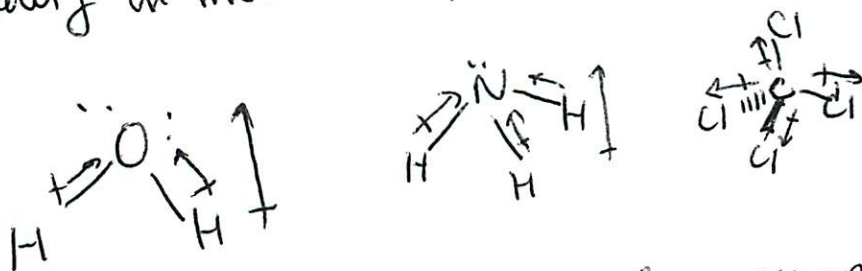
Compare $\text{I}-\text{Cl}$ to $\text{Br}-\text{Br}$

BP 97°C 59°C

$\text{Cl}-\text{Cl}$

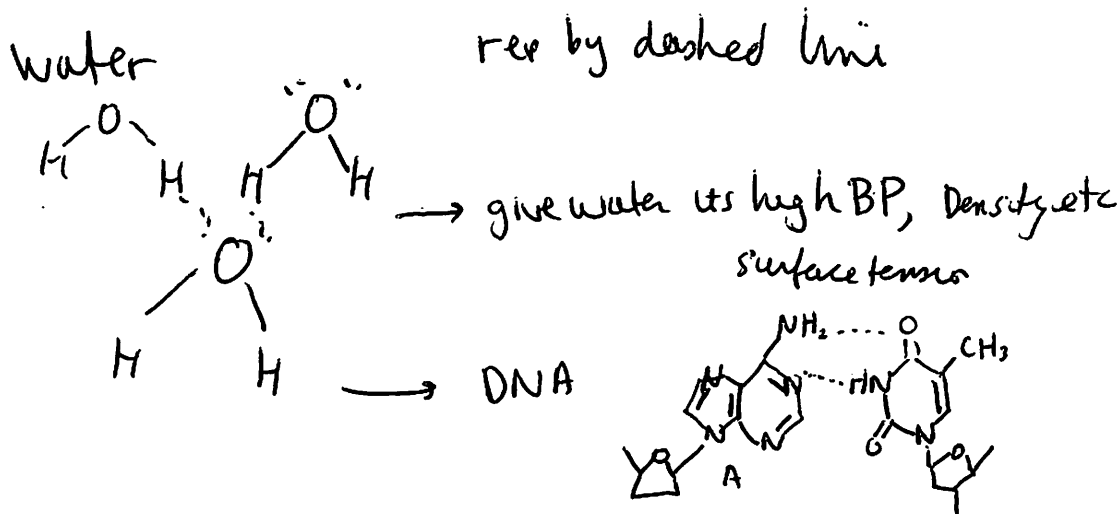


polarity in molecules - goes to more e^- neg atom

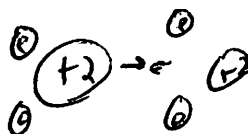
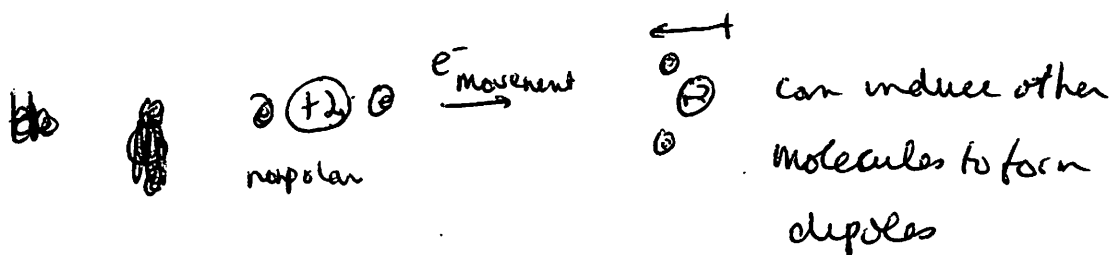


↳ can induce dipoles in nonpolar molecules

2. Hydrogen bonding - IM force attraction between an H bonded to a strong e⁻ negative atom + unshared pair of e⁻ on other strong negative atom



3. London dispersion forces → constant motion of e⁻ and creation of instantaneous dipoles and induced dipoles (always cap)



London higher in molecules w/ more e⁻

BP He -269

Ar -186 more e⁻ more LDF